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Dewatering Wastewater Treatment Sludge By Clathrate Freezing: A Bench-Scale Feasibility Study

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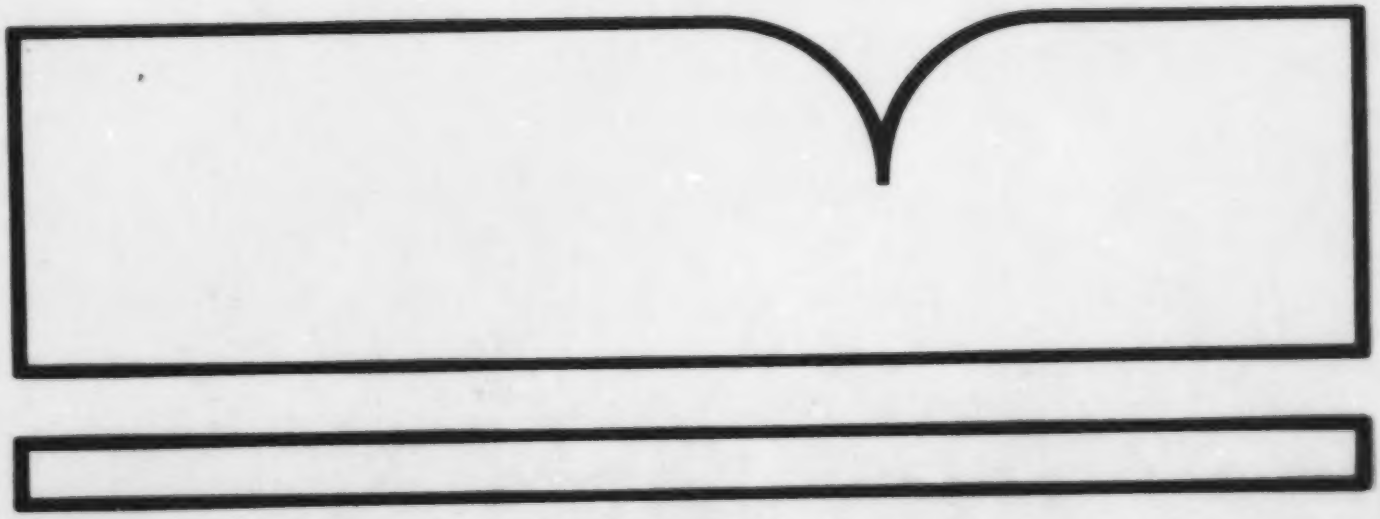

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DEWATERING WASTEWATER TREATMENT SLUDGE BY CLATHRATE FREEZING: A BENCH-SCALE FEASIBILITY STUDY

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Cooperative Agreement
No. CR 810549

Project Officer

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Cincinnati, Ohio 45268

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16. ABSTRACT

Laboratory studies were performed to prove the concept and feasibility for a novel technology to dewater wastewater treatment sludges. The technology involves the formation of solid hydrate crystals of water and specific clathrate-forming agents followed by separation of the hydrate crystal solids from the sludge solids, thereby producing a sludge solids mass depleted of water content. The objectives of the program also included obtaining preliminary data for dewatering wastewater sludges from the Millcreek Wastewater Treatment Plant in Cincinnati, Ohio.

Laboratory tests were performed using Freon-11 as clathrate-forming agent, in a bench-scale batch mode.

The objectives of the program were achieved, thereby demonstrating the technical feasibility of the concept.

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides formal communication between the researcher and the user community.

This report relates the results of a preliminary investigation of technical feasibility for a noval freezing process to dewatering wastewater treatment sludges. The technology, when further developed, may have the potential for simplifying and reducing the costs of sludge handling and disposal.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

Laboratory studies were performed to prove the concept and feasibility for a novel technology to dewater wastewater treatment sludges. The technology involves the formation of solid hydrate crystals of water and specific clathrate-forming agents followed by separation of the hydrate crystal solids from the sludge solids, thereby producing a sludge solids mass depleted of water content. The objectives of the program also included obtaining preliminary data for dewatering wastewater sludges from the Millcreek Wastewater Treatment Plant in Cincinnati, Ohio.

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The objectives of the program were achieved, thereby demonstrating the technical feasibility of the concept.

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SECTION 1

INTRODUCTION

According to the U.S. Environmental Protection Agency (EPA), in 1979 15,600 municipal wastewater treatment plants discharge about 6.5 million tons/year of solids (dry basis) in treated sewage sludge destined for some sort of disposal. In many cases, major U.S. municipalities are disposing of a very watery sludge (up to 98% water) because of inadequate technology, cost considerations, and a variety of local problems associated with more extensive dewatering. Sludge processing, dewatering, and disposal are major problems involving the use of various technologies to minimize environmental impacts.

The City of Cincinnati's Millcreek Wastewater Treatment Plant currently produces treated sewage sludge at the rate of 3,000 wet tons per day, which amounts to 1.095 million tons annually. Of this total, 1.058 million tons are water. The potential cost reductions from improved dewatering technology are so great that local governments could initiate the process and quickly recover their capital costs without relying on federal funds.

The purpose of this project was to perform laboratory-scale feasibility studies of the CLATHRATE process, a hydrate crystal forming process for sludge dewatering. The objectives of the studies were to prove the concept of the technology and obtain preliminary data for dewatering wastewater sludges from the Millcreek Wastewater Treatment Plant. Tests were performed with Freon-11 at atmospheric pressure, and only in a batch mode during the course of this particular project.

BACKGROUND

The U.S. Environmental Protection Agency (EPA) has issued in 1979 a process design manual that covers a contemporary review of sludge processing technology, including dewatering. In another publication (1980) devoted to plant operator training, the EPA covers the operational aspects of dewatering. These two publications, as selected examples, make it clear that sludge processing, dewatering, and disposal are major problems involving the use of various technologies to minimize environmental impact.

The most difficult technical obstacle to reducing sludge disposal costs is the reduction of the associated large water content. Again, sludge may contain as much as 98 percent water by weight. The CLATHRATE process involves the use of materials that form hydrate crystals with water. These crystals can be separated from sludge solids by physical means to achieve dewatering. Many elements and compounds have been found to form hydrate crystals with water above the freezing point of water. These hydrating

agents are readily available (propane and Freon-11, for example), and they can be recovered from the hydrate crystal phase and reused, thereby further reducing processing costs. A conceptual process block diagram for the dewatering process is presented in Figure 1.

Propane as a hydrating agent possesses the following desirable features:

1. Propane is inexpensive.
2. The rate of hydrate formation is satisfactory.
3. Formation conditions of temperature and pressure are economically attractive.
4. Propane has very low solubility in water.
5. Propane can be used as a direct heat transfer medium, thereby eliminating the use of heat exchangers to remove the heats of hydrate formation and decomposition. In a scaled-up plant design, propane would probably be the hydrating agent of choice. as it has the ability to break the cell walls of organisms, extract fats and lipids, and make the moisture within the cell available for hydrate formation. This particular activity with regard to the use of propane would, in fact, disinfect the sludge. An additional advantage of propane as a dewatering agent for wastewater treatment sludges is that the fats, greases, and oils dissolved by the propane do not interfere with the molecular formation of hydrate crystals, and these fats, oils, and greases may be readily recovered from the liquid propane by a simple flash operation.

For this study, however, Freon-11 was chosen and tests were performed in a batch mode because a less expensive, nonpressurized apparatus could be used to establish proof of principle. Experiments to determine yields and efficiencies should be performed using propane in a pressurized apparatus.

BENCH-SCALE STUDY OBJECTIVES

The goals of the feasibility study were to obtain data with Freon-11 for dewatering wastewater sludges from the Millcreek Wastewater Treatment Plant in Cincinnati, Ohio. The two primary technical issues addressed are: (1) the extent of clathrate formed, and (2) the degree of phase separation. These technical feasibility questions were addressed by performing Tasks 1 through 3 below:

TASK 1: Set up a bench-scale apparatus for obtaining basic clathrate formation process data.

TASK 2: Using the bench-scale apparatus described under Task 1, evaluate Freon-11 in tests with three available municipal sludges from the Millcreek Wastewater Treatment Plant (primary, secondary, and a mixture of primary and secondary).

TASK 3: Prepare a final report describing the results, conclusions, and recommendations from the bench-scale feasibility study for dewatering available municipal sludges from the Millcreek Wastewater Treatment Plant by using Freon-11 in the clathrate process.

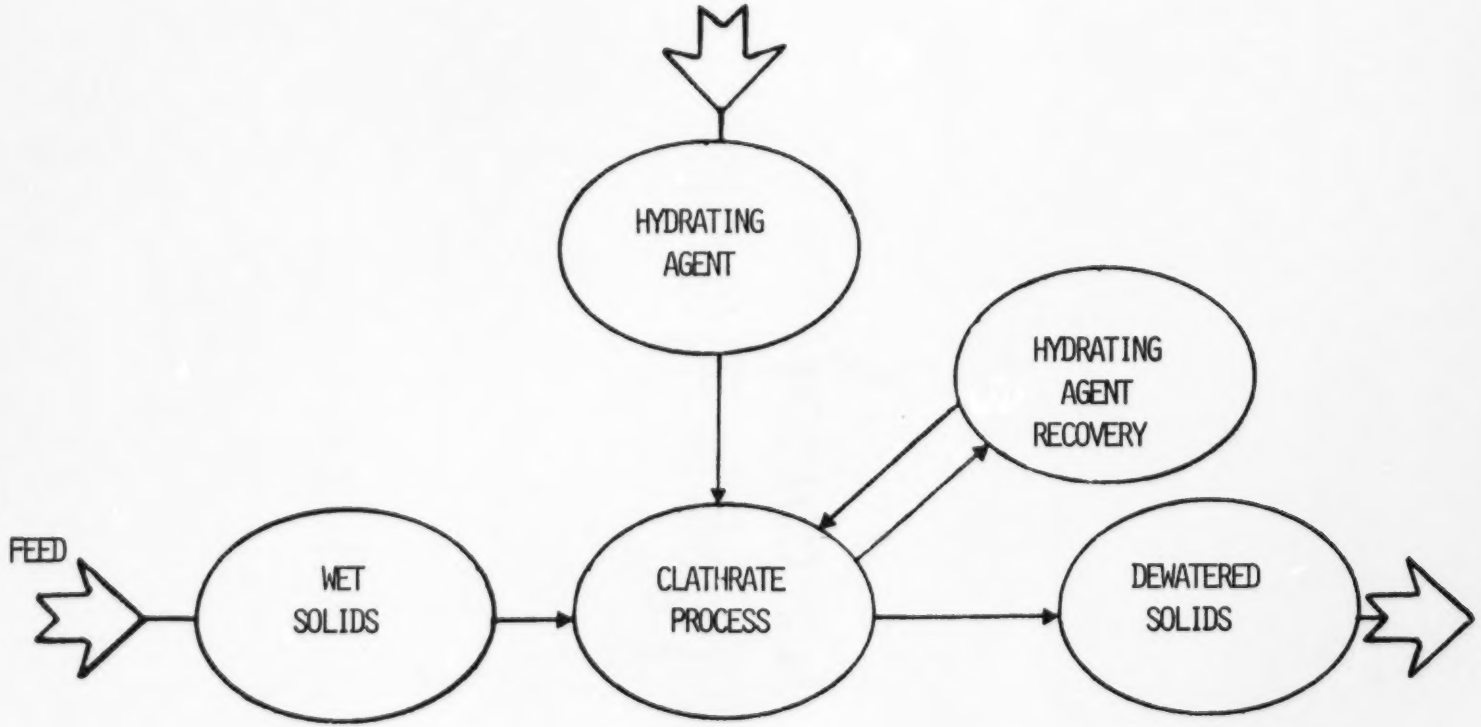


Figure 1. Process block diagram for dewatering wet solids.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. This study proved the concept that sludges may be dewatered by forming clathrate (hydrate) compounds of water with organic clathrating agents (Freon-11).
2. A crystalline hydrate of water can be obtained that may be separated from the treated sludge.
3. Multistaging (repeated contacts with clathrating agents) improves sludge dewatering.
4. Increasing the residence time increases water removal as hydrate crystals.

RECOMMENDATIONS

1. As the next logical step forward, sludge dewatering data should be taken while using propane as the hydrating agent and by performing the experiments in a large-size hydrate former vessel.
2. The extent of separation of crystalline hydrates from sludge solids should be investigated during testing with propane in larger size equipment.
3. The effect of residence time on water removal should also be investigated during testing with propane in a larger hydrate former vessel.
4. An experimental program should include the establishment of critical parameters and test and sampling procedures so that the data of all relevant variables can be ascertained.
5. The process should be optimized at the 100 gallon scale.
6. All wetted surfaces should be precoated in the reaction vessel to reduce the possibility of crystal deposition on such surfaces.
7. Economics for a full-scale process should be projected.

SECTION 3

RESULTS AND DISCUSSION

Testing was performed with Freon-11 as the hydrating agent and in a batch mode because no pressurized apparatus is required, and thus program costs could be held down. In a scaled-up plant design propane would probably be the hydrating agent of choice. Propane as a hydrating agent possesses the following desirable features: it is inexpensive; the rate of hydrate formation is satisfactory; formation conditions of temperature and pressure are economically attractive; it has a very low solubility in water; and it can be used as a direct heat transfer medium thereby eliminating the use of heat exchangers to remove the heats of hydrate formation and decomposition.

In Figure 2, the phase diagram of the Freon-11 water hydrate, or clathrate crystal system, indicates formation of a crystalline structure with water at a temperature as high as 46°F (8°C) and an equilibrium pressure of about 8.1 psia. At 34°F (1°C), the phase equilibrium condition is about 3.3 psia for the clathrate. The clathrate cystal consists of one molecule of Freon-11 surrounded by molecules of water which trap the hydrate agent forming a unit cell. The water tied up in the crystal is pure water and dissolved solids play no part in the crystalline structure.

Twenty exploratory test runs were initially performed in order to select suitable test procedures and operating conditions for use during actual tests. Emphasis was placed on determination of a procedure which would result in representative data for the sludge/Freon-11 test system. Effort was primarily placed on sampling techniques and obtaining suitable test conditions for forming Freon-11 hydrate crystals with all the free Freon-11 in the sample. Selected tests were also performed under inert nitrogen gas environment and at various impeller speeds. Generally, experimental results were very sensitive to the presence of free Freon-11 in samples. Initial experiments indicated 100% water removal. This was later attributed to presence of free Freon-11 in the samples. Subsequent experiments were greatly improved by tying up all of the free Freon-11 in Freon-11 hydrate form with the water vapor in the surrounding air. The technique used was to hold the sludge sample taken from the experiment above the cold reactor to give excess freon an opportunity to equilibrate with moisture in the air. Equilibrium was assumed to take place after several marked physical changes had taken place. The appearance of the excess freon in the sample was first clear, then slushy, progressing to crystalline white, next to milky and dry looking. Finally the entire sample became friable. Each sample was allowed to progress through these changes before being removed for weighing. Similar changes also occurred in the samples of pure clathrate which were used to determine the water to freon ratio of the clathrate alone.

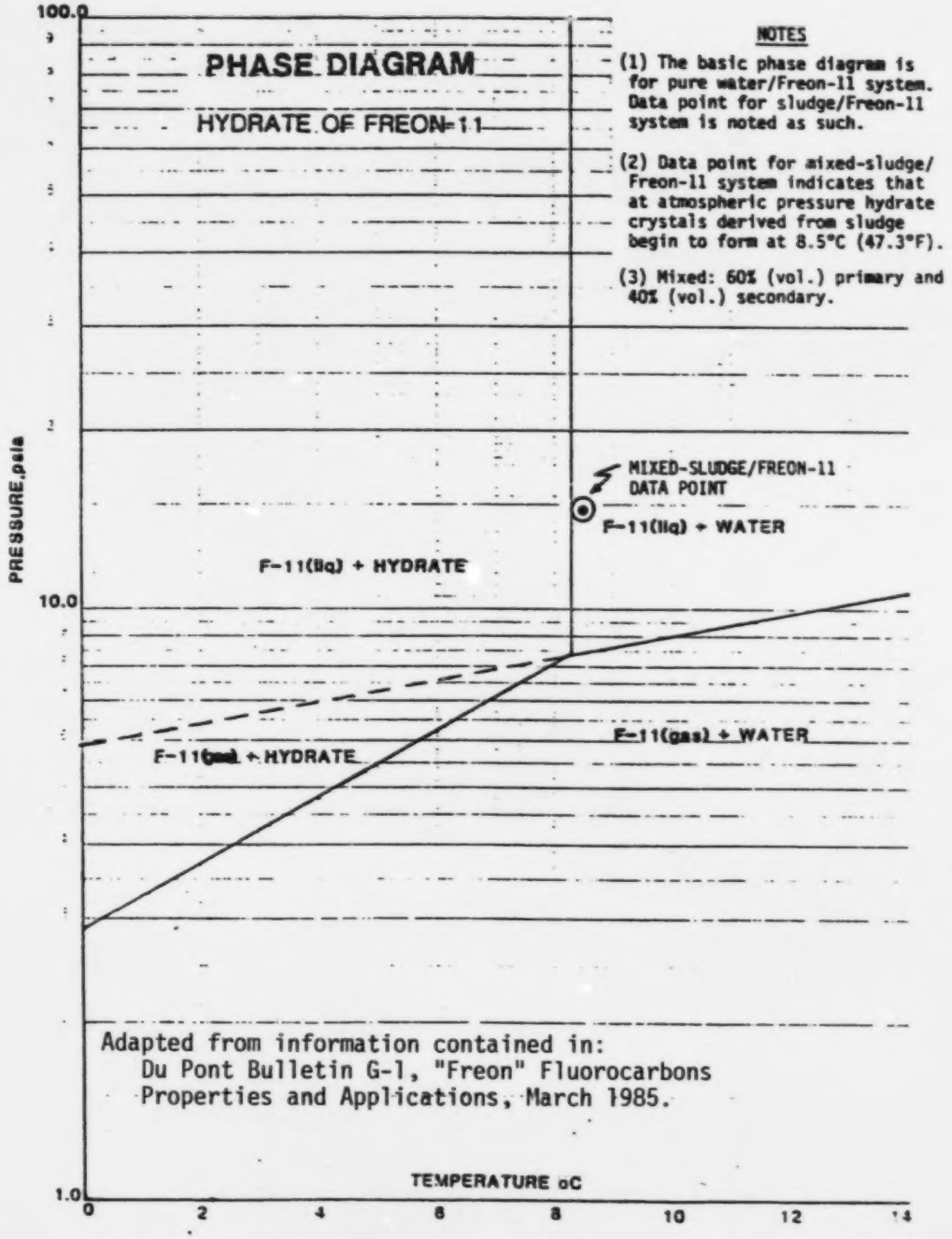


Figure B-1. Phase diagram.

An important consideration in the evaluation of the test data was the type of Freon-11 hydrate crystals. Two types of Freon-11 hydrate crystals were actually observed. One type was grayish in color and very soft with a molar ratio measured in unpublished previous BENMOL studies of approximately 17 to 1 (water to Freon-11). The second type of crystals obtained by more extended contacting was bright white and very hard with a molar ratio of approximately 7 or 8 to 1. During final experiments the more easily separated second type of Freon-11 cystals were obtained by using sufficient contacting. The procedures finally selected and used during the actual tests involving the second type of crystals are in Appendix A. Included in this Appendix are: apparatus preparation, sample preparation, and initial moisture analysis, charging the reactor, conducting tests, sampling, moisture analysis, two-stage tests, daily sludge control, and sludge sample collection.

Actual testing was performed with samples of primary, secondary activated, and a mixture of 60% (vol.) primary and 40% (vol.) secondary activated sludges from the Millcreek Wastewater Treatment Plant. The final test matrix and corresponding results for the second type crystals are presented in Table 1. Test data presented here were collected using the experimental apparatus shown in Figure 3. Selected photographs taken during the experiments are shown in Figure 4. Detailed test results, again obtained with the second type crystal, are in Appendix B. Included in this Appendix are: detailed sludge dewatering data, data for molar ratio of water to Freon-11 in the hydrate crystals, and the phase diagram for the 60% (vol.) primary and 40% (vol.) secondary activated sludge mixture/Freon-11 system. As is evident from the data obtained, both objectives of the program were achieved thereby demonstrating the technical feasibility of the concept.

Several papers relating to crystallized design were also reviewed. Theoretically, the population density for a continuous crystallizer: (1) operating steadily, (2) thoroughly mixed and discharging a representative sample, (3) that is unseeded and/or where particles formed by attrition are of negligible size, and (4) where growth of the crystals follows the Delta L law, has been shown by Randolph and Larson (1962) to be:

$$n = n^{\circ} \exp(-L/Gt) \qquad (1)$$

where

n = population density, no/mm
L = crystal length, mm
G = growth rate, mm/hr
t = retention time, hr
n° = intercept at $L = 0$

Nothing in Equation 1 incorporates features unique to the mechanical design of different scale crystallizers or crystallizers operating at different pump speeds which can produce significantly different product sizes. Historically, the result of increased pump speed is increased nucleation rate or smaller product crystals. Bennett et al. (1973) presented a theoretical basis for this observation structuring their derivations on the work of Clontz and McCabe (1971) which indicated that contact with a crystal growing in a supersaturated solution produced nuclei in proportion to the energy of the striking force and the contact area. Bennett et al. (1973) presented the following equation for the nucleation rate:

$$Be^\circ = k\rho G\ (TIPS^2/TO)M_4 \qquad (2)$$

where

Be° = nucleation rate, no/hr
k = a constant
ρ = density of the solution, g/cm^3
G = growth rate, mm/hr
TIPS = tip speed of the propeller or impeller, m/s
TO = crystallizer turnover time, in s, crystallizer volume/circulation rate
M_4 = fourth moment of the crystal distribution $= \int_0^\infty nL^4 dL$

Bennett et al. (1973) found the following correlation for NaCl crystallization.

$$Be^\circ = k\ (TIPS^2/TO)^{0.97}\ G^{0.98}\ M_4^{0.84} \qquad (3)$$

Bennett (1983) correlated the data for sodium carbonate monohydrate crystallization with the following equation:

$$Be^\circ = k\ (TIPS^2/TO)^{1.15}\ GM_2 \qquad (4)$$

where

M_2 = second moment of crystal distribution $= \int_0^\infty nL^2 dL$

Although the objectives of the program were achieved thereby demonstrating the technical feasibility of dewatering sludges from the Millcreek Wastewater Treatment Plant, the scope of this project did not provide for a detailed investigation. It would be highly desirable to investigate crystal formation in detail and compare the significant findings with: (1) published correlations such as presented above, (2) data from small scale and pilot plant test programs such as presented in a recent article by Garside and Shah (1980), and (3) published data from commerical size crystallizers employing a variety of pump speeds.

TABLE 1. FINAL TEST MATRIX AND RESULTS (TEMP. 1.5°C)

Test System	Residence Time (Mins.)	Water Removed[1] (Wt% of Total)
Primary Sludge/Freon-11	10	48.0
	>10	92.3
	20 (Staged)[2]	50.6
	>20 (Staged)[2]	93.4
Secondary Activated Sludge/Freon-11	10	76.4
	>10	97.9
60% (vol.) Primary and 40% (vol.) Secondary Activated/Freon-11	10	64.7
	>10	90.1

(1) Average Values
(2) Normally, ten minutes residence time for each of two contact stages.

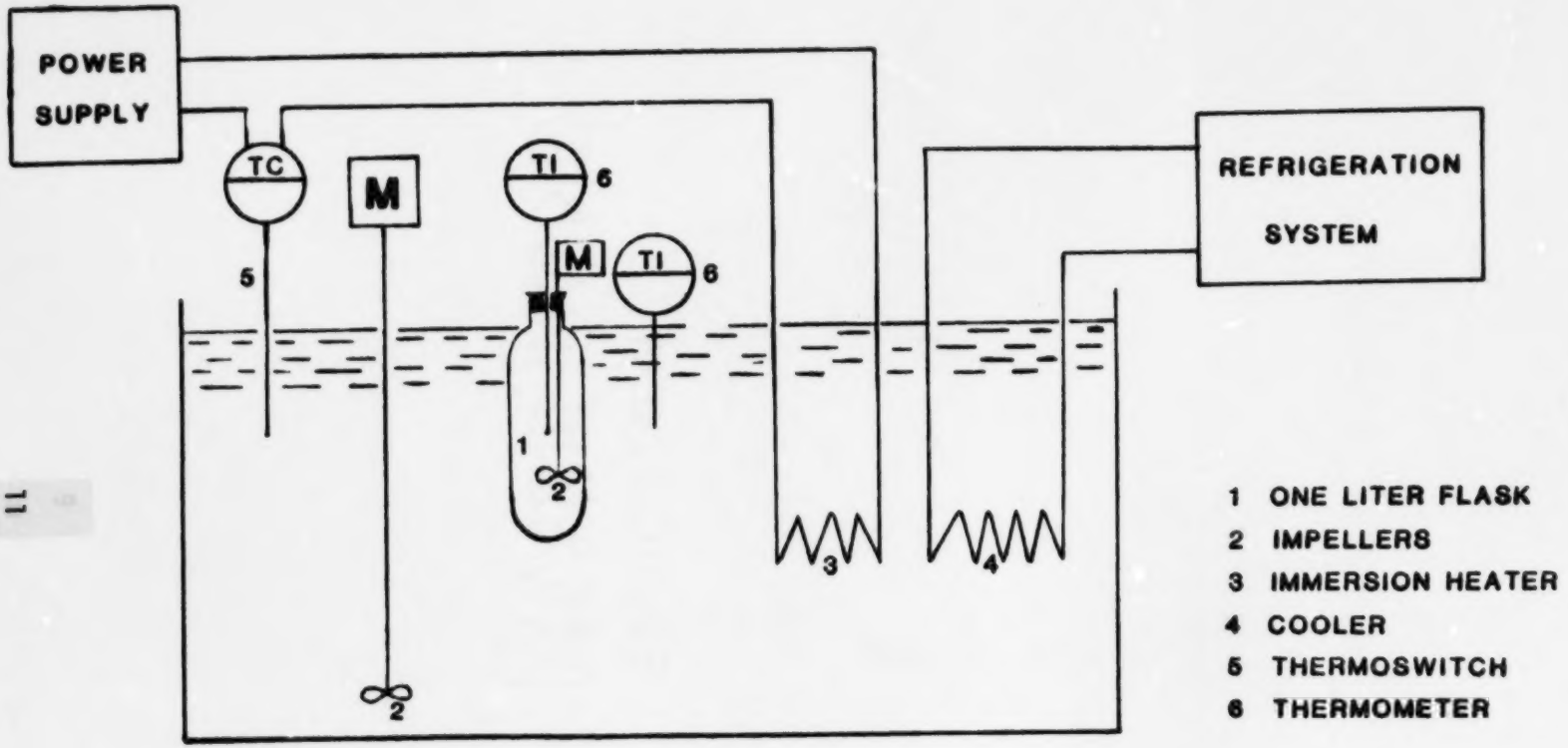
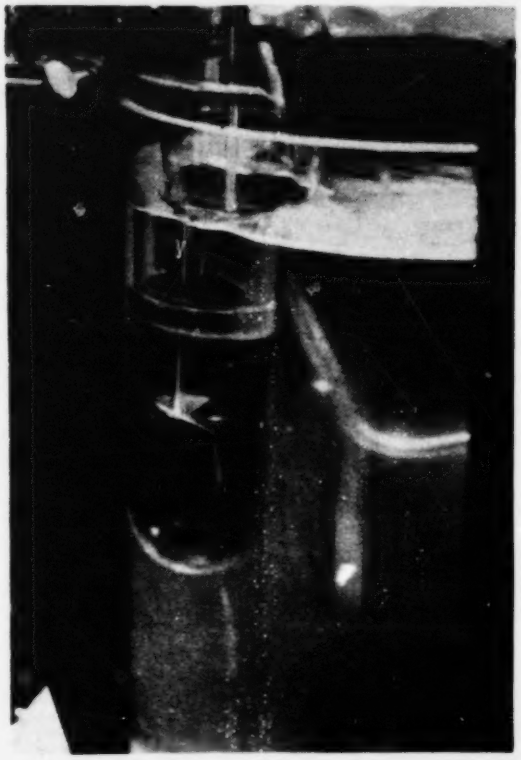
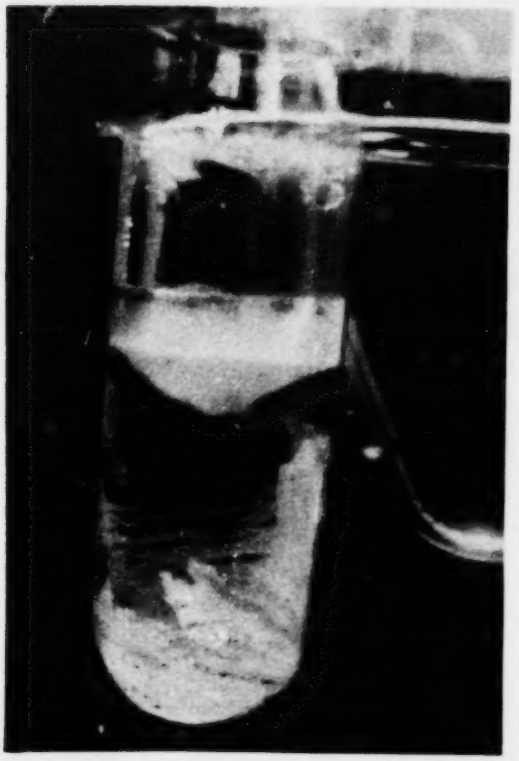


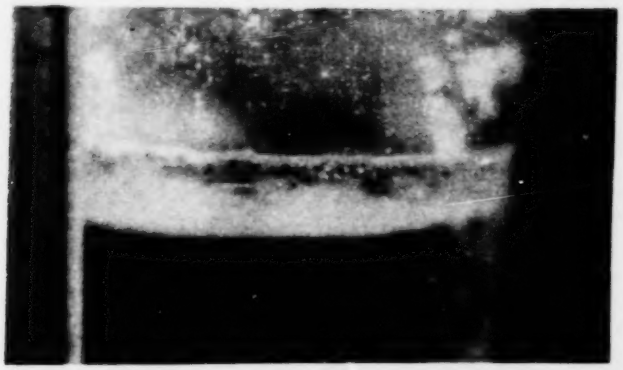
Figure 3. Dewatering apparatus.



Beginning of a Test Run



Conclusion of a Test Run



Close-Up of Hydrate Crystals (Bottom)/Dewatered Sludge (Top) Layers at Conclusion of a Test Run

Figure 4. Photographs taken during typical experiments.

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APPENDIX A

TEST PROCEDURES

The test and sampling procedures are combined below in a series of experimental steps which guided the data collection.

APPARATUS PREPARATION

1. Set the bath temperature to 1.5°C. Ensure the bath temperature has stabilized before proceeding.
2. Dry two sampling vials, 25 ml each, with their caps in an oven at 103°C for one hour.
3. Remove the vials and caps from the oven and place into a desiccator for one hour.
4. Weigh the vials with the matching caps.

SAMPLE PREPARATION AND INITIAL MOISTURE ANALYSIS

5. Select the sludge sample to be tested from the final test matrix. Obtain the indicated sludge from the refrigerated container with appropriate label.
6. Vigorously shake the sludge storage container permitting a homogeneous sample to be withdrawn. Withdraw two 10 g samples, and place into aluminum dishes. Dry these samples at 103°C for four hours, then weigh after keeping in the desiccator for one hour to determine the initial moisture content.
7. Vigorously shake the sludge container and pipet 20 ml of well mixed sludge (40 ml sludge sample for the activated secondary) from the center of the container using a large bore pipet. Hold until procedure 12.

CHARGING THE REACTOR

8. Measure 500 ml of refrigerated Freon-11 in a one liter graduated cylinder. Pour all of the Freon-11 into the reaction vessel which has been immersed in the water bath.
9. Insert the impeller of the reactor mixing device with an aluminum foil lid (4" x 4" on its shaft) at one-half the occupied depth of the filled reaction chamber. Mold the foil lid around the top of the vessel.
10. With the variable transformer at 100/120 setting, engage the mixer and stir the Freon-11 in the vessel for one minute to cool it to the bath temperature.

11. Disengage the mixer.
12. Dispense the measured amount of sludge sample into the reaction vessel containing the 500 ml Freon-11.
    Pipet 0.3 cc* surfactant (0.6 cc* surfactant for secondary activated sludge) into the reaction vessel and its contents.
13. Insert the impeller of reactor mixing device again with the aluminum foil lid on the shaft of the impeller at one-half the occupied depth of the filled reaction chamber. Mold the foil lid around the top of the vessel.

START TEST

14. With the variable transformer setting at 100/120, engage the mixer and continue stirring for the duration of the test time indicated on the final test matrix shown in Table B-1. During the runs performed with the activated secondary sludge, stop the mixing after five minutes and pipet 0.3 ml* more surfactant into the reaction vessel and its contents by first disengaging and then engaging the impeller as explained above. Then continue mixing with the transformer at 120/120 setting.
15. Monitor the bath temperature at five minute intervals. Record the bath temperature readings on the operations log sheet. Adjust the thermostat as necessary to obtain desired temperature.

TEST COMPLETED

16. Disengage the mixer at the completion of the test interval.
17. Remove the mixing apparatus and aluminum foil from the reactor.
18. If the Freon-11 hydrate crystals are not formed, bubble air through the Freon-11 using a pipet and pipet filler. Keep bubbling the air until all of the free water in sludge is crystallized.
19. Wait until the Freon-11 hydrate and sludge solids phases separate.
20. Record the appearance of physical separation of Freon-11 hydrate crystals and sludge solids.

SAMPLING

21. Immerse the bottom half of a sample vial in the water bath, and keep it immersed during the sampling.
22. Using a stainless steel spatula remove about 0.2 gr sample from the sludge solid phase located at the top phase in the reactor. Hold the sample right above the sampling vial in the air until all of the free Freon-11 forms Freon-11 hydrate crystals with the moisture in the air and drops freely into the sampling vials. Repeat this operation until there is enough sample at the bottom of the vial.
23. Close the vial with its screw-cap very tightly while the vial is immersed in the water bath.

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*Experimentally optimized quantity to give the best phase separation in the Bench-Scale equipment.

24. Remove the vial and its contents from the water bath, and wipe off the outside with a paper towel.
25. Repeat procedures 21 through 24 with the second vial to obtain a second sample.
26. Wait until the sample vials warm up to room temperature.
27. Place the vials into the desiccator for one hour, then weigh.

MOISTURE ANALYSIS

28. Open the caps of the vials, and immerse the vials in a 35°C water bath to vaporize Freon-11.
29. Cap the vials and wipe off with a soft paper towel.
30. Place vials in a desiccator for one hour, then weigh.
31. Open the caps of the vials and place the vials and their caps in an oven at 103°C for four hours.
32. Close the caps of the vials and place into a desiccator for one hour, then weigh.

TWO-STAGE TESTS

Tests are to be performed as described in the above procedures, with the following exceptions:

- Conduct the first run for ten minutes.
- After the first ten minute experiment, remove most of the sludge solid phase and place into a beaker. Let the beaker warm up to the room temperature. Charge a fresh reactor with the sample in the beaker. However, use only 0.1 ml of surfactant in the new charge.
- Conduct second run for ten minutes.
- Carry out moisture analysis.

DAILY SLUDGE CONTROL

Moisture analyses are performed, as previously indicated on the original sludge batch, each day testing is conducted.

SLUDGE SAMPLE COLLECTION

- Sludge samples are collected at Millcreek Sewage Treatment Plant.
- Twenty-four hour composite samples of primary and secondary activated sludges are collected in six pint-size containers.
- Samples are delivered to Millcreek Plant Laboratory on the day of sample collection.
- Six containers are mixed together to produce one homogeneous batch of sludge. A new four pint-size (approximately) sludge mixture which consisted of 60% (vol.) primary sludge and 40% (vol.) secondary activated sludge, is prepared by homogeneous mixing of the proper amounts of prepared primary and secondary activated sludges. The sludge is transferred back to the pint-size containers for refrigerated storage.
- Sludge samples are refrigerated allowing one sludge batch to be used for a four week test period.

- All remaining sludge samples are stored at 4°C for 60 days after test completion.

APPENDIX B

DETAILED TEST RESULTS

A total of twelve final experiments were performed with sludges obtained from the Millcreek Wastewater Treatment Plant. Results of the dewatering experiments performed with primary, secondary activated, and mixed sludges are presented in Table B-1. An additional experiment was performed using distilled water and Freon-11 in order to determine the molar ratio of water to Freon-11 in the hydrate crystal structure. The data for this run is presented in Table B-2.

Reported percent final solids in Table B-1 were calculated as follows. The total mass of Freon-11 tied up in the Freon-11 hydrate crystal structure, in a fixed amount of sample, was initially determined. From this value and the mass of water per unit mass of Freon-11, from experimental data presented in Table B-2, the mass of water tied up in the crystal structure was calculated. Then from the moisture analysis, the mass of total amount of water and the mass of total amount of dry solids were determined. The percent final solids were calculated from the following equation:

$$\% \text{ Final Solids} = \frac{\text{Mass of Dry Solids}}{\text{Mass of Dry Solids + Excess Water}}$$

where the Excess Water is the difference between the mass of total water and the mass of water tied up in the Freon-11 hydrate crystal structure.

In Table B-1 the percent yield is defined to be the weight percent of the initial water removed from the sludge sample, and was calculated as follows.

Let

W_i = Weight of sludge before dewatering
W_f = Weight of sludge after dewatering
S_{ic} = Mass fraction of solids in the initial sample (corrected)
S_f = Mass fraction of solids in final sample

Assuming that removed water does not contain any solids, then

$$W_i \, S_{ic} = W_f \, S_f \qquad (1)$$

or

$$W_f/W_i = S_{ic}/S_f \qquad (2)$$

$$\underset{(\% \text{ Yield})}{\% \text{ Water removed}} = \frac{W_i(1-S_{ic}) - W_f(1-S_f)}{W_i(1-S_{ic})} \times 100 \qquad (3)$$

If the nominator and denominator of Equation (3) are divided by W_i and the value of W_f/W_i is substituted from Equation (2), then the following equation can be obtained.

$$\underset{(\% \text{ Yield})}{\% \text{ of Water removed}} = \frac{1 - S_{ic}/S_f}{1 - S_{ic}} \times 100 \qquad (4)$$

The phase diagram for 60% (vol.) primary sludge and 40% (vol.) secondary activated sludge mixture/Freon-11 system was presented in Figure 2.

TABLE B-1. DETAILED SLUDGE DEWATERING DATA. PERCENT OF THE INITIAL WATER REMOVED BY FREON-11 HYDRATE FORMATION (TEMP. 1.5°C)

Run No.	% Initial Solids (Average) (100. S_i)	% Corrected* Initial Solids (100. S_{ic})	% Final Solids (100. S_f)	%Yield[1] $\frac{1-S_{ic}/S_f}{1-S_{ic}} \times 100$
PRIM-1a	7.03	7.28	54.03	93.32[2]
PRIM-2a	7.03	7.28	47.27	91.24[2]
PRIM-3a	7.03	7.28	17.45	62.86
PRIM-3b	7.03	7.28	14.73	54.55
SPRIM-4a/1	7.35	7.60	20.27	67.65
SPRIM-4b/1	7.35	7.60	20.83	68.74
SPRIM-4a/2	20.55	20.60	24.23	18.78/74.28[4]
SPRIM-4b/2	20.55	20.60	56.56	80.07[3]/93.68[4]
SPRIM-5a/1	7.55	7.79	9.21	16.72
SPRIM-5b/1	7.55	7.79	9.28	17.41
SPRIM-5a/2	9.25	9.34	10.59	13.02/28.67[4]
SPRIM-5b/2	9.25	9.34	14.16	37.55/48.79[4]
SPRIM-5c/2	9.25	9.34	55.10	91.64[3]/93.14[4]
SEC-1a	1.55	2.05	18.85	90.99
SEC-1b	1.55	2.05	15.71	88.77
SEC-2a	1.80	2.29	3.95	43.00
SEC-2b	1.80	2.29	7.10	69.33
SEC-2c	1.80	2.29	19.01	90.02
SEC-2d	1.80	2.29	52.57	97.88[2]
MIX-1a	5.65	5.93	37.30	89.40[2]
MIX-1b	5.65	5.93	40.50	90.74[2]
MIX-2a	5.30	5.58	11.50	54.52
MIX-2b	5.30	5.58	15.35	67.41
MIX-3a	5.15	5.43	17.52	72.97
MIX-3b	5.15	5.43	13.78	64.07

PRIM - Primary sludge.
SPRIM - Staged-runs with primary sludge.
Note: Staging enhanced water removal.
SEC - Secondary activated sludge.
MIX - 60% (vol.) primary sludge and 40% (vol.) secondary activated sludge mixture.

1 - Values are for 10 minute and 20 minute (staged) runs, unless noted otherwise. Time per stage is 10 minutes.
2 - Longer than 10 minute run.
3 - Longer than 20 minute run.
4 - Overall yield.

* - Analytical corrections due to non-volatile matter in surfactant (from experimentally measured residue)

TABLE B-2. MOLAR RATIO OF WATER TO FREON-11 IN THE HYDRATE CRYSTAL STRUCTURE (TEMP. 1.5°C)

Sample No.	Moles Water/Mole Freon-11
1	7.5820
2	8.0034
3	6.8111
4	8.0824
Average.	7.6197
Standard Deviation . . .	0.5822

APPENDIX C

DESCRIPTION OF MILLCREEK WASTEWATER TREATMENT PLANT

The Millcreek Wastewater Treatment Plant is the largest of the major wastewater treatment plants operated by the Metropolitan Sewer District of Greater Cincinnati for the Hamilton County Commissioners.

The Millcreek Treatment Plant, initially providing chemically assisted primary treatment of wastewater with chlorination, separate sludge digestion, vacuum filtration, and incineration, was completed in 1959. It was constructed on a land area of 76 acres with future expansion in mind.

Hydraulic design is based on a dry weather flow of 120 million gallons per day with facilities for handling a maximum of 360 million gallons per day of combined wastewater and storm flow. It has a service area of approximately 133 square miles and serves over a half million persons. The wastewater and industrial wastes received at the Millcreek plant are from the highly industrialized Millcreek Valley.

Expansion of the Millcreek plant to secondary treatment using activated sludge was completed in 1978. It is designed to produce an effluent containing not more than 23 mg/l of bio-chemical oxygen demand, 30 mg/l of suspended solids and 10 mg/l of total Kjeldahl nitrogen. Chlorination facilities for disinfection purposes have been provided.

APPENDIX D - Addendum

This addendum has been prepared by a report reviewer in order to present an expanded explanation of the procedure used by the authors to determine the moisture remaining in the sludge solids after contact with Freon-11. The reviewer disagrees partially with the explanations offered by the authors of what occurs when a sample is withdrawn from the Freon-sludge contact vessel, but agrees that the procedure may yield a valid estimate of the moisture remaining in the sludge.

The authors state (Results and Discussion, par. 3, refer also to Appendix A, Test Procedures, Items 21-23) that incorrect results were obtained in their estimate of water in the sludge until they developed a procedure for eliminating the free Freon-11 in their sample of the sludge-clathrate layer. In this procedure, the sample is held over the sample bottle until water from the air converts all of the Freon-11 to clathrate, at which point the mass becomes grainy and freely falls from the spatula into the sampling vessel. This reviewer thinks that the explanation given is incomplete. Moisture from the air converting Freon-11 to clathrate is not the only phenomenon that seems to be occurring. In the following, the sampling procedure is reviewed and explained further and the method of calculating sludge moisture content is illustrated.

Sludge and Freon-11 are contacted in a well-mixed contactor for at least 10 minutes, mixing is then stopped, and the phases are allowed to separate. The mixture separates into a lower layer containing the liquid Freon-11 and an upper layer containing sludge solids (with some residual water), clathrate crystals, and liquid Freon-11. The location of this mixture on the water-Freon-11 phase diagram just before sampling is shown in Figure D-1 as point 1 (the presence of sludge solids can be ignored in this discussion). Freon-11 liquid, Freon-11 gas, clathrate (or hydrate) are present. The Freon-11 gas is exerting its vapor pressure of about 6.3 psia (the Freon-11 gas does not escape because the vessel is covered).

When the sample on the spatula is removed from the contacting vessel, it is held over the sampling vial, which is partially immersed in the 1.5°C water bath. The sample receives some heat from the ambient air surrounding it, but it is still cold. The Freon-11 liquid present on the sample has a vapor pressure of 6.3 psia. Two processes will immediately take place - the liquid Freon-11 will start to evaporate rapidly, and the moisture in the air will condense on the cold object. Liquid Freon-11 is lost by two processes - evaporation and combination with moisture from the air to form clathrate. Evaporation is likely the dominant mechanism because a pressure driving force of 6.3 psi is substantial. Probably cooling of the sample to substantially below 1.5°C occurs, caused by the need to supply latent heat to evaporate the Freon-11.

The net result of these two mechanisms is the "drying up" of the sample. All liquid Freon-11 disappears and only clathrate and the residual sludge solids remain on the spatula. Referring to Figure D-1, the mixture is now at point 2 (approximately, since the temperature is not accurately known).

If the mixture at point 2 were allowed to remain in the air at this point, the clathrate, which is in equilibrium with Freon-11 gas and which

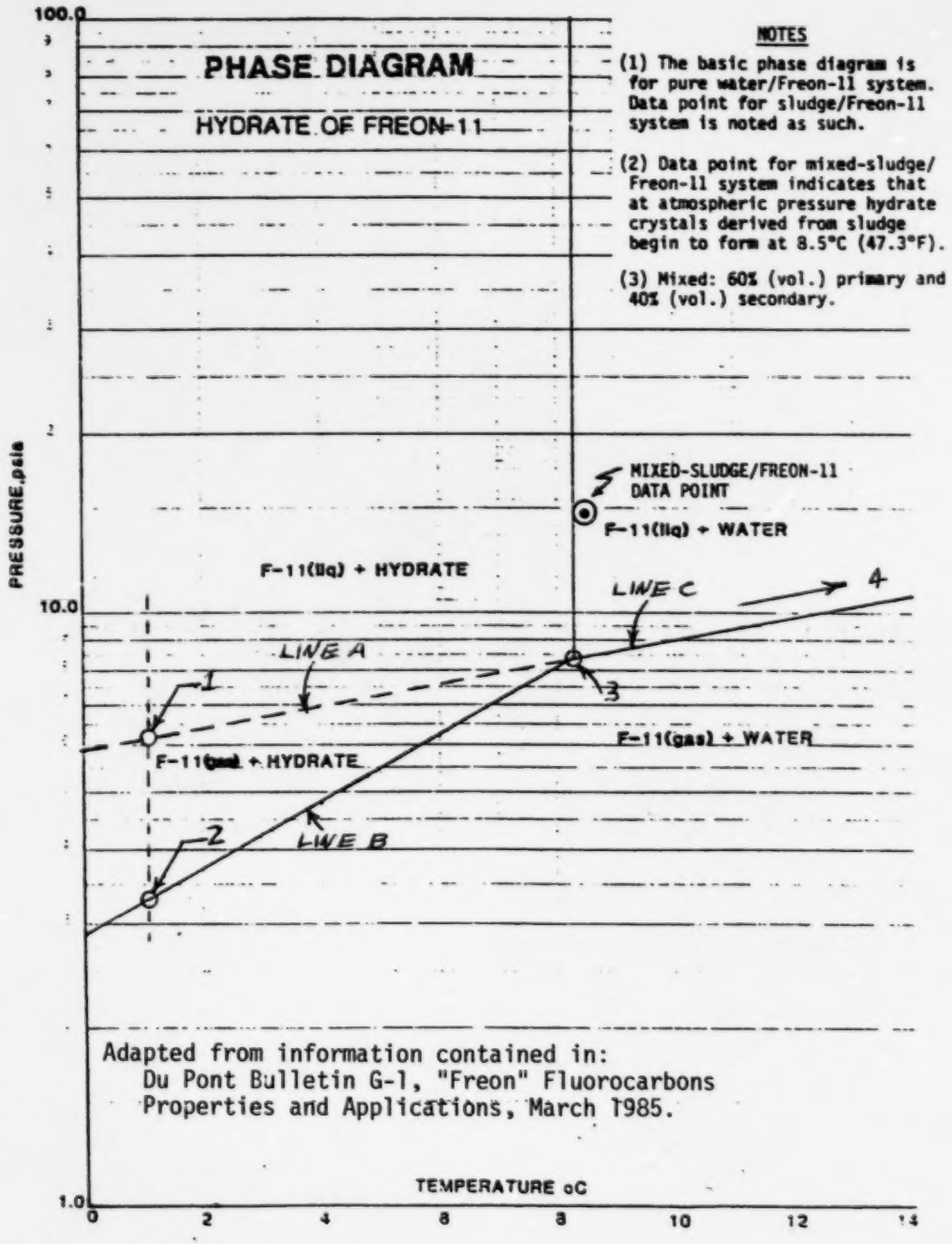

Figure B-1. Phase diagram.

is exerting a Freon-11 vapor pressure of about 3.3 psia at this point, would lose Freon-11 and would gradually decompose, releasing Freon-11 gas and liquid water. Evidently this did not occur because the authors claimed that the material which slid or was dropped into the sampling vial appeared to be dry.

The sample vial is tightly capped so as the sample warms to room temperature, Freon-11 gas pressure increases. The path is along Line B to point 3. At this point, the clathrate crystals decompose to Freon-11 liquid, Freon-11 gas, and water. With further warming, the sample travels along Line C towards point 4 at room temperature. When the sample is analyzed for moisture (see Appendix A, Test procedure, Items 26-32), the sample vial is weighed, giving total sample mass. Then the vial is uncapped and heated to 35°C. Freon-11 liquid and vapor are removed in this step. An unknown amount of water vapor is lost in this step, swept out with the escaping Freon-11 gas. Although the vapor pressure of water is small compared to the total pressure, it is not trivial at 35°C (H_2O vapor pressure is 42 mm Hg)*. The sample vial is then weighed, giving total Freon-11. The vial is next heated to 110°C to remove water and weighed. Residual mass is dry sludge solids, which is determined by a final weighing.

The moisture content in the residual sludge solids is calculated as follows:

Let M = Total mass of sample

F = Mass of Freon-11

L = Total mass of water

S = Mass of sludge solids

X = Mass of water associated with clathrate

Y = Mass of water associated with sludge solids

M, F, L, and S are determined by direct weighing.

Mass of water associated with the clathrate is found from F and the ratio of Freon-11 to water in the clathrate.

*The weight ratio of water to Freon in the escaping gas would be approximately

$$\frac{42(18)}{(760-42)(137.88)} = 0.00764$$

From Table B-2, moles water/mole Freon-11 = 7.62.

$$\frac{\text{Mass water}}{\text{Mass Freon}} = \frac{(7.62)(18)}{137.38} = 0.998$$

(Freon-11 is CCl_3F, MW = 137.38

$X = (F)(0.998)$

Therefore $Y = L - X = L - 0.998\ F$

$$\text{Moisture content of sludge solids (\%)} = \frac{Y}{(S + Y)} \times 100$$

Summary Comment: The method for determining moisture content of sludge solids appears reasonable and is consistent with anticipated behavior. However the method depends on the following assumptions which have not been verified: (1) The endpoint - when all Freon-11 adhering to the sample has either been converted to clathrate or has evaporated and no decomposition of clathrate to Freon and water has occurred - can be accurately identified just by visual inspection of the sample, (2) moisture loss in the Freon-11 evaporation step (evaporation at 35°C) is negligible, and (3) the clathrate compound always has a mole ratio of 7.62 moles water/mole of Freon-11**. The manner in which moisture content of the sludge is calculated also introduces uncertainty. The mass of moisture in the sludge, Y, is the difference between two numbers, L and X (see above) which are both large relative to Y. Errors in X or L will be magnified in the calculation of Y. Systematic errors (e.g., the aforementioned evaporation of water when the Freon-11 is boiled off at 35°C) might pass unnoticed since they would not inflate the standard deviation in sludge solids moisture content as much as random errors. An independent determination of sludge solids, achievable only by first separating sludge solids from clathrate crystals, is needed before it can be confidently asserted that the authors' procedures have yielded reliable results.

Reviewer: Joseph B. Farrell

**Project Officer Comment: The mole ratio was measured in independent experiments using only pure water and Freon-11. It is doubted that the crystalline structure of clathrate would differ significantly when sludge is an additional component. The stoichiometry of distinct crystalline phases is usually constant. Under both conditions, the appearance of the crystals and the procedure used to obtain them were similar.